

Electro-deposited Sol-gel Coatings Containing Ceramic Nanocontainers Loaded with Inhibitors for the Corrosion Protection of AA2024-T3

E.D. Mekeridis¹, I.A. Kartsonakis^{*2}, G. Kordas³

Sol-Gel Laboratory, Institute of Advanced Materials, Physicochemical Processes, Nanotechnology and Microsystems, NCSR 'DEMOKRITOS', 15310 Agia Paraskevi, Greece

¹emekeridis@ims.demokritos.gr; ^{*2}ikartsonakis@ims.demokritos.gr; ³gkordas@ims.demokritos.gr

Abstract

This study reports the application of sol-gel coatings on aluminium alloy 2024-T3 substrates under electrochemical regimes and dip-coating process. Cerium-titanium oxide nanocontainers loaded with corrosion inhibitors 2-mercaptobenzothiazole and 8-hydroxyquinoline were incorporated into the coatings in order to improve the corrosion protection properties. Various silanes and silicones were used as precursors. The electro-deposited coatings were compared to coatings developed by dip coating process. Electrochemical impedance spectroscopy measurements were carried out in order the corrosion protection properties of the films to be evaluated. It was found that 3-glycidoxypyltrimethoxysilane based films provided better protection against corrosion. The presence of nanocontainers improved the corrosion protection.

Keywords

Sol-Gel; Electro-Deposition; Nanocontainers; Corrosion; EIS

Introduction

During the last years, lots of scientific interest has been focused on the replacement of conventional corrosion inhibitor, such as Cr(VI). The reason is that Cr(VI) provokes serious human diseases [1]. Several alternatives have been proposed ranging from the incorporation of various other inhibitors in the conversion or the primary coating [2, 3], to the use of organic or inorganic coatings giving strong barrier properties [4, 5] and from special surface pre-treatment such as plasma ablation [6] or anodisation [7] to the application of conducting polymer layers [8-9].

Despite the fact that alternatives to chromates are still not efficient enough, experiments on the combination of two, three or more processing techniques are under

investigation in order the most promising candidate for the replacement of chromium to be found. Under this scope, conducting polymers have been doped with inhibiting molecules [10], sol-gel films have been developed with encapsulated inhibitors [11, 12] and various deposition techniques have been applied [13].

Cerium compounds belong in the category of the most promising alternatives to chromates. A considerable amount of references can be found in the literature concerning its corrosion protection properties [14]. Corrosion inhibition, by cerium salts is generally associated with the formation and precipitation of cerium oxides or hydroxides over cathodic sites on the metal surface. These precipitates give rise to a blocking effect and reduce the rate of reduction reactions. Pepe et al. [15] have demonstrated that cerium incorporation in a sol gel film may inhibit the corrosion reaction by migrating through the coating to the site of the attack and then react to passivate this site.

2-mercaptobenzothiazole (2MB) and 8-hydroxyquinoline (8HQ) were studied as corrosion inhibitors for aluminium alloys (AA) 2024-T3 by Lamaka et al. [16]. They found that these inhibitors provide anticorrosion protection for AA2024-T3 forming a thin organic layer of insoluble complexes on the surface of the alloy. K.A. Yasakau et al. examined the addition of 8HQ at different stages of the synthesis process to understand the role of possible interaction of the inhibitor with the components of the sol-gel system [17]. 2MB was evaluated by Zheludkevich et al. as corrosion inhibitor for protection of AA2024-T3 in neutral chloride solutions [18].

The sol-gel technique consists in a sequence of hydrolysis and condensation reactions giving rise to a rigid polymer network with some very interesting properties which may also be altered by enclosing different types of molecules in the network [19]. Its insulating character makes them very attractive to corrosion science as they can be applied onto metallic substrates providing a strong barrier protection against corrosion. Sol-gel coatings are usually applied on the surfaces either by spin coating, or dip coating. A less known method is electro-deposition or more likely electro-condensation. This method of a sol-gel coating application has already been reported in the literature mainly concerning silane type coatings developed on different conducting surfaces including pure aluminium [20, 21]. The procedure is based on the application of a cathodic potential which generates a local increase of pH near the electrode surface. The synthesized hydroxyl and hydrogen ions from H₂O reduction act as catalysts in the condensation and hydrolysis process, respectively, results in the controllable sol-gel film deposition.

We report here on the possibility of electro-depositing onto AA2024-T3 substrate a silane sol-gel coating doped with cerium. This deposition technique provides coatings with high cerium concentrations because the cerium salt performs as the electrolyte during deposition process. Different silane precursors were examined. Ceramic nanocontainer reservoirs loaded with 2MB and 8HQ were incorporated into the sol-gel matrix in order to improve the corrosion protection. Release studies of the inhibitor of these nanocontainers are presented in our previous work [22]. We studied a variety of nanocontainers concentration in solution. The resulting coatings are compared to those developed by dip coating method. The curing treatments of the coatings were conducted below the temperature at which the organic inhibitors are decomposed.

Experimental

Materials and Reagents

AA2024-T3 panels were used for all the experiments with the nominal mass composition depicted in Table 1. All chemicals were of analytical reagent grade. 8-hydroxyquinoline (8HQ, Sigma-Aldrich, St. Louis, USA), cerium nitrate (Ce(NO₃)₃, Sigma-Aldrich, St. Louis, USA), sodium chloride (NaCl, Aldrich), (3-

Glycidoxypyl)trimethoxysilane (GPTMS, Across Organics), Diethoxydimethylsilane (DEDMOS, Sigma-Aldrich, St. Louis, USA), Trimethoxymethylsilane (TMOMS, Sigma-Aldrich, St. Louis, USA) absolute ethanol (Aldrich), were used without further purification. All solutions were freshly prepared prior to use with distilled, deionised water.

TABLE 1 THE % W/W NOMINAL COMPOSITION OF AA2024-T3

Element	Al	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
% w/w	90.7-94.7	< 0.5	< 0.5	3.8-4.9	0.3-0.9	1.2-1.8	< 0.1	< 0.25	< 0.15

Coating deposition

AA2024-T3 panels were purchased by EADS (Germany) and cleaned before use by etching for 3 min in a 2% NaOH solution at 40°C. After that, the panels are rinsed with distilled water and are inserted into 4.33 M solution of HNO₃ for 1 minute at room temperature. Finally, they are rinsed with distilled water.

The deposition process includes an electrolytic solution consists of siloxane monomer, ethanol and water in a 4:4:1 molar ratio. Silanes GPTMS and TMOMS and silicone DEDMOS were used as precursors. The mixture was stirred for 1 h at 40°C in order hydrolysis to occur. Ce(NO₃)₃*6H₂O in concentration 0.1 M was used as the electrolyte for the electro-polymerisation process [17, 18]. Different concentrations of the electrolyte (Ce(NO₃)₃) in the range of 0.05 M to 0.5 M were also studied without satisfied results. The cerium salt was added before application of the potential in order to minimise formation of cerium oxide. Then, loaded cerium-titanium (Ce-Ti) oxide nanocontainers were added to the solution, under vigorous stirring, before the coating process.

A three electrode electrochemical cell was used connected to a Solartron 1287 PGstat. The cleaned aluminium panel was the working electrode, a platinum sheet the counter electrode and a SCE electrode served as reference. Electro-deposition took place under potentiostatic regime applying a cathodic potential of 1.4 V vs SCE (saturated calomel electrode) for 30 min. After deposition, the samples were dried in various temperatures. Moreover, for comparison reasons, a series of coated samples with the same thickness were also prepared from the described

solutions, using the dip coating process. The panels were dip coated four times into the solutions with a withdraw speed of 10.5 cm/min. Each time, the panels remained in the solution for 1 min.

Characterization

The morphology of the coatings was determined by scanning electron microscopy (SEM) using a PHILIPS Quanta Inspect (FEI Company) microscope with W (tungsten) filament 25 KV equipped with EDAX GENESIS (AMETEX PROCESS & ANALYTICAL INSTRUMENTS). Furthermore, the coatings were characterized by Reflectance Infrared Spectroscopy using a Perkin Elmer universal ATR sampling accessory spectrum 100 FT-IR spectrometer.

The corrosion resistance of the coatings was studied by electrochemical impedance spectroscopy (EIS) using a SI 1287 Solartron Electrochemical interface connected with a SI 1260 Impedance/gain-phase analyzer. The experiments were performed at room temperature, in a Faraday cage, at the open circuit potential, using a three-electrode electrochemical cell, consisting of working electrode ($\approx 2 \text{ cm}^2$ of exposed area), saturated calomel electrode (SCE) as reference and platinum as counter electrode. The measuring frequency ranged from 50 kHz to 5mHz. For every result, a minimum of 3 repetition measurements were taken. Spectra were treated using the Z-view Software using the adequate equivalent electric circuits.

The experimental data were fitted using an appropriate equivalent circuit model. Instead of capacitances Constant Phase Elements (CPE) were used in all fittings procedures because the phase angle of the capacitor is different from -90° [12]. The impedance of the CPE depends on frequency according to the following equation

$$\frac{1}{Z} = Q(j\omega)^n \quad (1)$$

where Z is the impedance, Q a parameter equals to $(1/|Z|)$ at $\omega=1 \text{ rad s}^{-1}$, ω is the frequency and $n \leq 1$ a power coefficient calculated as ratio of phase angle at maximum of corresponding time constant to -90° . The capacitance values for coating, oxide and double layer elements can be calculated using the equation:

$$C = Q(\omega_{\max})^{n-1} \quad (2)$$

where $\omega_{\max}$ is the frequency at which the imaginary impedance reaches a maximum for the respective time constant.

Results and Discussion

Cerium-Titanium oxide nanocontainers

Cerium titanium oxide nanocontainers were synthesized through a two-step process and then loaded with corrosion inhibitors 2-MB and 8-HQ. The synthesis, characterization and the loading process of these nanocontainers are reported in our previous work [22]. The nanocontainers exhibit an average diameter of $180 \pm 10 \text{ nm}$ and they are 4.37 % w/w loaded with 8HQ and 25.36% w/w with 2-MB.

Coatings

Siloxanes are divided to three categories, silicones, silanes and silicates, according to the number of alkoxy-groups they have. DEDMOS and TMOMS form a siloxane network through hydrolysis of the methoxy/ethoxy groups on the silane followed by condensation of the silanol groups to form siloxane bonds. The application of a cathodic potential results in the controllable sol-gel film deposition. Thereby, a covalently bonded interpenetrating network is formed. Although GPTMS follows a similar mechanism, this precursor includes in his structure one epoxy ring [23]. The importance and activity of epoxy rings, is due to the big tendency of split of the ring. The bond angles of the epoxy ring are roughly 60° , which is considerably smaller than the regular tetrahedral angle of 109.5° of carbon, or the 110° angle of bivalent oxygen of open chain ethers. As long as the atoms cannot be regulated so as to allow wider orbital cover, the bonds are weaker than usual ether and the molecule is less stable. According to Morisson and Boyd, epoxy rings are catalyzed by acid with great facility and can be split by base too [24].

As it was reported above, electro-deposition is based on the application of a cathodic potential which generates a local increase of pH near the electrode surface due to reduction of H_2O [17, 18]. The increase of the hydroxyl and hydrogen ions from H_2O reduction act as catalysts in the condensation and hydrolysis process, respectively. The epoxy ring is split by ethanol solvent resulting in the formation of a more dense coating with increased corrosion protection properties [25].

Thickness of the coating

Coating thickness based on GPTMS is proportional to the time of electro-deposition (table 2). Fig. 1 presents the SEM image of the cross section of the coatings that were

TABLE 2 THICKNESS OF THE GPTMS COATINGS

Coating	Temperature	Thickness (μm)
Electrodeposited	Room	~4.3
Dip coated (1 dip)	Room	~3.0
Dip coated (4 dips)	Room	~4.0
Electrodeposited	90°C for 24 hours	~2.7
Dip coated (1 dip)	90°C for 24 hours	~1.1
Dip coated (4 dips)	90°C for 24 hours	~3.9

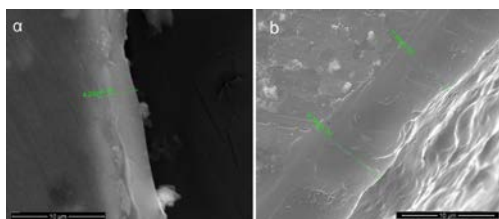


FIG. 1 SEM IMAGES OF COATINGS SYNTHESIZED WITH TIME OF ELECTRO-DEPOSITION A) 30 MIN., B) 60 MIN

prepared by electro-deposition and dried at room temperature. It is clearly seen that the increase of electro-deposition time corresponds to an increase of the thickness of the coatings. More specific, an increase of time from 30 min to 60 min doubled the thickness of the coatings (from $\sim 4\mu\text{m}$ to $\sim 8\mu\text{m}$).

Morphology of the coatings

SEM and EDX analysis were used in order the morphology and the element composition of the coatings to be determined. Fig. 2 illustrates the GPTMS based coated samples (electro-deposited or dip coated) after drying at 90 °C for 24 hours. Both methods provided smooth and homogeneous coatings without cracks. EDX analysis confirmed the application of the coating on the substrate due to appearance of carbon, oxygen and silicon. Aluminium and copper elements are from the substrate.

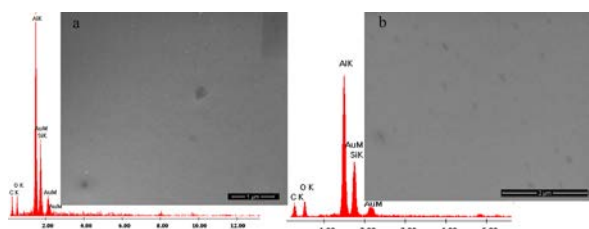


FIG. 2 SEM IMAGES OF THE GPTMS A) ELECTRO-DEPOSITED B) DIP COATED SAMPLES AFTER DRYING AT 90 °C FOR 24 HOURS

All samples reported here were dried at 90 °C for 24 hours. Fig 3 and 4 present DEDMOS and TMOMS based coatings. DEDMOS based coatings show defects for both coating methods. TMOMS based coatings

formatted with the electro-deposition process are homogeneous. It can be seen from SEM images that electro-deposition provides more homogeneous coatings compare to coatings formatted with the dip coating process where defects are appeared. Coatings based on GPTMS lasted longer into the corrosive environment while coatings based on DEDMOS and TMOMS were degraded.

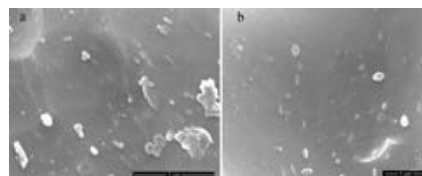


FIG. 3 SEM IMAGES OF THE DEDMOS A) ELECTRO-DEPOSITED B) DIP COATED SAMPLES AFTER DRYING AT 90 °C FOR 24 HOURS

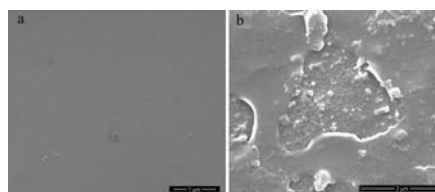


FIG. 4 SEM IMAGES OF THE TMOMS A) ELECTRO-DEPOSITED B) DIP COATED SAMPLES AFTER DRYING AT 90 °C FOR 24 HOURS.

Figs. 5 and 6 demonstrate the electro-deposited GPTMS based coatings with loaded nanocontainers before and after exposure to corrosive environment. No significant differences are observed for both coatings after the incorporation of loaded nanocontainers. Both coatings are smooth and no defects can be observed. After 72 hours of exposure to corrosive environment, cracks appear leading to the degradation of the coatings.

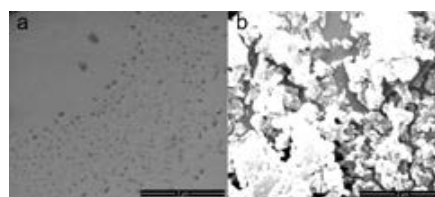


FIG. 5 SEM IMAGES OF THE ELECTRO-DEPOSITED COATING WITH CE-TI NANOCONTAINERS LOADED WITH 8HQ (A) BEFORE AND (B) AFTER 72 HOURS OF EXPOSURE IN 0.05 M NACL SOLUTION.

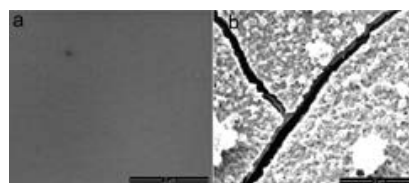


FIG. 6 SEM IMAGES OF THE ELECTRO-DEPOSITED COATING WITH CE-TI NANOCONTAINERS LOADED WITH 2MB (A) BEFORE AND (B) AFTER 72 HOURS OF EXPOSURE IN 0.05 M NACL SOLUTION.

Fig. 7 illustrates the mapping of the coated sample with the nanocontainers. As long as cerium element presents into the coating due to its addition into the solution as $\text{Ce}(\text{NO}_3)_3$, the distribution of the cerium titanium oxide nanocontainers can be estimated by the titanium element. Spots of titanium can be clearly seen to the images of all the coatings. This proves that the Ce-Ti nanocontainers are uniformly distributed in all coatings.

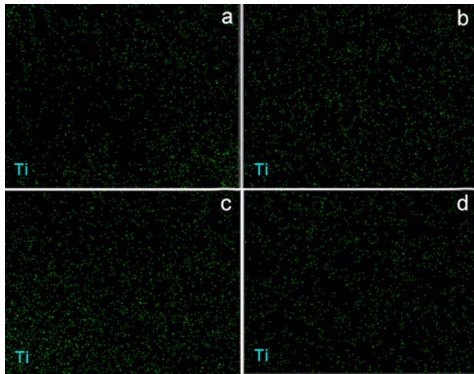


FIG. 7 MAPPING SEM OF GPTMS A) DIP COATED B) ELECTRO-DEPOSITED COATING WITH CE-TI NANOCONTAINERS LOADED WITH 8HQ C) DIP COATED D) ELECTRO-DEPOSITED COATING WITH CE-TI NANOCONTAINERS LOADED WITH 2MB.

Corrosion Resistance Testing

Fig. 8 presents the Bode plots of electro-deposited and dip coated samples based on different precursors (DEDMOS, GPTMS and TMOMS). These coated samples were cured in air at room temperature or at 90 °C, and they were exposed at 0.05 M NaCl solution at room temperature for 72 hours. It can be seen from these plots that only GPTMS based coated samples present a time constant at high frequency region. This time constant cannot be seen very well because the silane oxide barrier properties appear at higher frequencies than 10^5 Hz. The absence of barrier properties for all the other coated samples denotes that the coatings maybe have pores, cracks or defects that make the electrolyte ions and the water molecules to penetrate into them and reach easily the metal substrate. On the other hand, the Bode plots of all the coatings present time constant in the range of $5 \cdot 10^{-1}$ to 10^1 Hz, due to the formation of aluminium oxide layer between the substrate and the coating. However, the Bode plots of all the coatings reveal signals of corrosion activity by the presence of time constant at 0.02 Hz. The impedance at low frequencies corresponds to the polarisation resistance of the coated samples and therefore can be used to estimate the corrosion protection [16, 26]. The values of the total

impedance for the DEDMOS and TMOMS based coatings are about the same as the bare AA2024-T3 after 72 hours of immersion into the corrosive environment, revealing that these coatings cannot protect the substrate from corrosion attack. On the other hand, heat treated electro-deposited GPTMS based coating presents better corrosion performance than all the other coatings as it has higher values of total impedance.

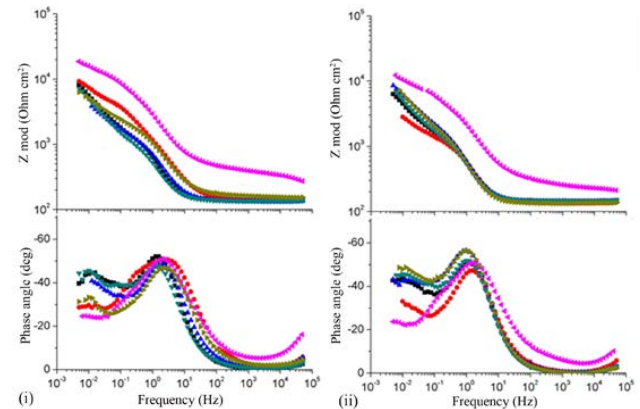


FIG. 8 EIS BODE PLOTS OF THE I) ELECTRO-DEPOSITED II) DIP COATED SAMPLES BASED ON A) (■) DEDMOS (●) GPTMS (▲) TMOMS DRIED IN AIR AT ROOM TEMPERATURE AND B) (▼) DEDMOS (◀) GPTMS (▶) TMOMS DRIED AT 90°C, AFTER EXPOSURE AT 0.05 M NaCl SOLUTION AT ROOM TEMPERATURE FOR 72 HOURS.

Fig. 9 depicts the behavior of GPTMS based coatings during time of exposure at 0.05 M NaCl solution. Both coating methods reveal total impedance values one order of magnitude higher than the bare AA2024-T3 after 24 hours of immersion.

According to EIS results the best coatings were GPTMS based coatings after curing at 90 °C. In order to improve the corrosion protection properties of these coatings, nanocontainers loaded with inhibitors were incorporated into these coatings in different concentrations. Different concentrations of loaded nanocontainers were studied. Figs. 10 and 11 present the Bode plots for the GPTMS based coatings, electro-deposited or dip coated, with different content of loaded nanocontainers. No improvement on the corrosion protection is demonstrated for the dip coated coatings with the addition of different amounts of loaded nanocontainers. On the contrary, the increase of the percentage of the nanocontainers into the electro-deposited coating leads to an increase of the total value of impedance. Thus, better corrosion protection is achieved. The total impedance is raised to values up to one order of magnitude higher than the bare AA2024-T3 for coatings with 0.1 % w/v of

nanocontainers loaded with 8HQ for the GPTMS based electro-deposited coatings (Fig. 10).

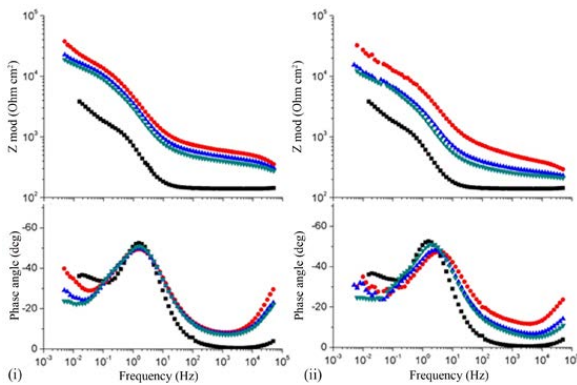


FIG. 9 EIS BODE PLOTS OF GPTMS BASE COATED SAMPLES I) ELECTRO-DEPOSITED II) DIP COATED SAMPLES AFTER EXPOSURE AT 0.05 M NaCl SOLUTION AT ROOM TEMPERATURE FOR (●) 24, (▲) 48 (▼) 72 HOURS AND (■) BARE AA2024-T3 AFTER 72 HOURS OF EXPOSURE.

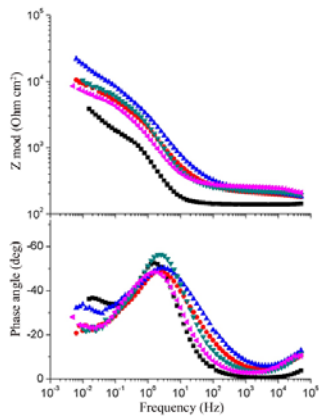


FIG. 10 EIS BODE PLOTS OF (■) BARE AA2024-T3, GPTMS ELECTRO-DEPOSITED SAMPLES INCORPORATING NANOCONTAINERS LOADED WITH 8HQ (●) 0.05% W/V AND (▲) 0.1% W/V, AND GPTMS DIP COATED SAMPLES INCORPORATING NANOCONTAINERS LOADED WITH 8HQ (▼) 0.05% W/V (◄) 0.1% W/V, AFTER EXPOSURE AT 0.05M NaCl SOLUTION AT ROOM TEMPERATURE FOR 72 HOURS.

The increase of the percentage of the nanocontainers loaded with 2MB for GPTMS based coatings, electro-deposited or dip coated, does not present any improvement of the corrosion protection properties of these coatings (Fig. 11).

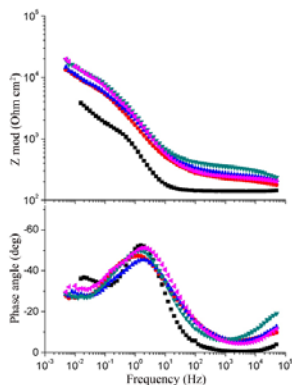


FIG. 11 EIS BODE PLOTS OF (■) BARE AA2024-T3, GPTMS ELECTRO-DEPOSITED SAMPLES INCORPORATING NANOCONTAINERS LOADED WITH 2MB (●) 0,05% W/V AND (▲) 0,1% W/V, AND GPTMS DIP COATED SAMPLES INCORPORATING NANOCONTAINERS LOADED WITH 2MB (▼) 0,05% W/V (◄) 0,1% W/V, AFTER EXPOSURE AT 0.05 M NaCl SOLUTION AT ROOM TEMPERATURE FOR 72 HOURS.

Figs. 12 and 13 present the behavior of GPTMS based electro-deposited and dip coated samples loaded with 0.1% w/v of nanocontainers after exposure to 0.05 M NaCl solution. All the coated samples present time constants at high frequency region (10^4 - 10^5 Hz) correspond to the barrier properties of the coatings. Moreover, all the coated samples demonstrate time constants at the medium frequency region due to the formation of aluminium oxides. The 24 and 48 hour plots present two time constants at the medium frequency region due to the formation of aluminium oxides and the formation of complexes between the inhibitor (that has been released from the nanocontainers) and the aluminium substrate. On the other hand, the low frequency time constants indicate that pitting attack exists, suggesting that corrosion activity could not be effectively inhibited. To sum up, the presence of the loaded nanocontainers enhances the barrier properties of the coatings and increases the overall impedance.

A more detailed analysis of the corrosion protection properties of different sol-gel coatings can be achieved by fitting the experimental data with an appropriate equivalent circuit model. The experimental impedance spectra were fitted using the equivalent circuit presented in Fig. 14. For the coatings loaded with nanocontainers, an equivalent circuit composed of 4 time constants is proposed.

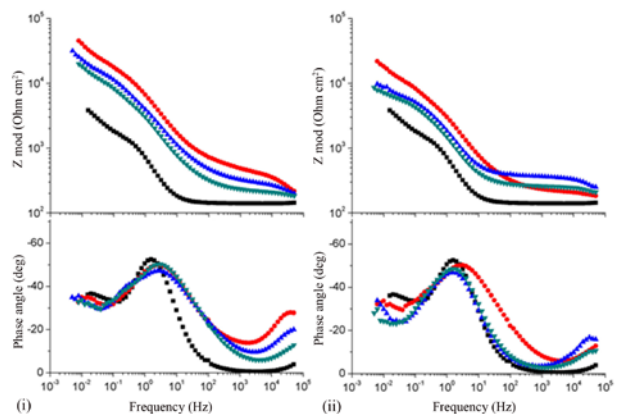


FIG. 12 EIS BODE PLOTS OF GPTMS I) ELECTRO-DEPOSITED II) DIP COATED SAMPLES INCLUDING 0,1% W/V NANOCONTAINERS LOADED WITH 8HQ, AFTER EXPOSURE AT 0.05 M NaCl SOLUTION AT ROOM TEMPERATURE FOR (●) 24, (▲) 48, (▼) 72 HOURS AND (■) BARE AA2024-T3 AFTER 72 HOURS OF EXPOSURE.

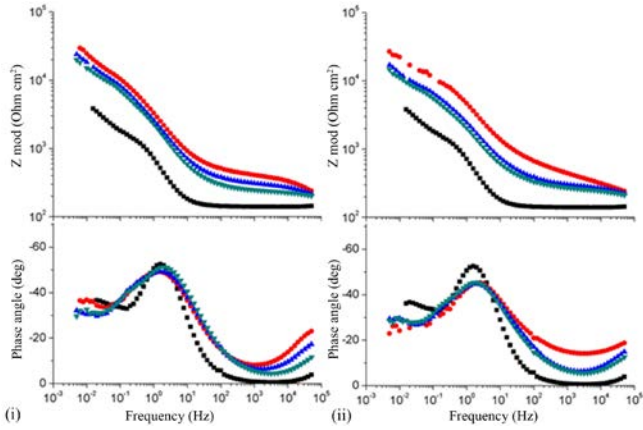


FIG. 13 EIS BODE PLOTS OF GPTMS I) ELECTRO-DEPOSITED II) DIP COATED SAMPLES INCLUDING 0.1% W/V NANOCONTAINERS LOADED WITH 2MB, AFTER EXPOSURE AT 0.05 M NaCl SOLUTION AT ROOM TEMPERATURE FOR (●) 24, (▲) 48 (▼) 72 HOURS AND (■) BARE AA2024-T3 AFTER 72 HOURS OF EXPOSURE.

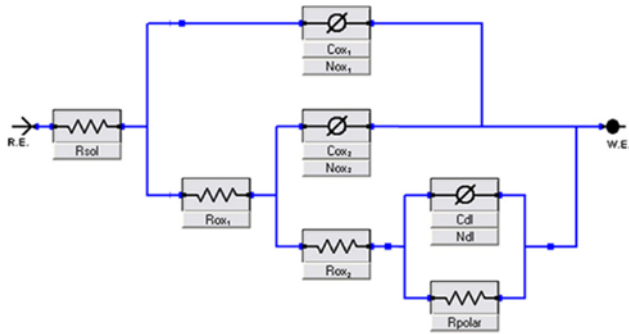


FIG. 14 THE EQUIVALENT CIRCUIT USED FOR FITTING EXPERIMENTAL EIS SPECTRA OF AA2024-T3 COATED SAMPLES.

R_{sol} is the resistance of the electrolyte. C_{coat} and n_{coat} are the parameters of constant phase element (CPE) describing the capacitance of the sol-gel coating. C_{ox1} and n_{ox1} are the parameters of constant phase element (CPE) describing the capacitance of the oxide layer, C_{ox2} and n_{ox2} are the parameters of constant phase element (CPE) describing the capacitance due to the intermediate layer that develops in the presence of inhibitor. C_{dl} and n_{dl} are the parameters of CPE which characterize the capacitance of the double layer [12, 25, 26]. It is clearly denoted that the best coating performance is provided by the coatings with 0.1 % w/v nanocontainers loaded with 2MB or 8HQ.

Figs. 15 and 16 present the evolution of different parameters after fitting of electro-deposited coatings and dip coated samples during time. The capacitance of the film depends on the amount of the absorbed water. Fig. 15a demonstrates the evolution of the film capacitance during immersion. The capacitance is

stable for the dip coated film including nanocontainers loaded with 8HQ taking values about $3 \times 10^{-8} \text{ F cm}^2$. The capacitances of the other coatings depict fluctuations. The resistance of the coating is determined by the resistance of the pores in the coating [26].

Hence, the evolution of the film resistance illustrates the barrier properties and stability of the layer during immersion. Fig. 15b presents the evolution of the coatings resistance during immersion in 0.05M NaCl solution. The R_{coat} for the electro-deposited coating with 8HQ loaded nanocontainers is the highest at early immersion stages (about $950 \Omega \text{ cm}^2$) but it is decreased after 48 hours of immersion. A stable behaviour of the pore resistance is observed during the next 72 hours taking values about $330 \Omega \text{ cm}^2$, which is roughly $100 \Omega \text{ cm}^2$ higher than the coating resistance of the dip coated samples and $50 \Omega \text{ cm}^2$ higher than the electro-deposited coating with 2MB loaded nanocontainers. This result reveals stronger barrier properties for the electro-deposited coating with 8HQ loaded nanocontainers.

The resistance R_{ox1} (Fig. 16a), which is associated to the aluminium oxide, is increased in the presence of the nanocontainers, reaching values of $29.6 \text{ k}\Omega \text{ cm}^2$ (electro-deposited) and $20 \text{ k}\Omega \text{ cm}^2$ (dip coating), for the coatings with nanocontainers loaded with 8HQ at early immersion stages. The resistance of the oxide is a measure of the interface stability and therefore inhibition ability. It is clear that the protection is much higher in the presence of the containers loaded with corrosion inhibitor. The resistance of the mid/low frequency time constant (R_{ox2} , Fig. 16b), which is the resistance of an intermediate layer that develops in the presence of inhibitor and appears only for the systems containing inhibitor is slightly lower than the oxide resistance. The presence of this time constant it intimately related with the presence of inhibitor, probably that inhibits active sites.

The polarization resistance provides information about the performance of the coating against corrosion and is related to the polarization phenomena in the pits formed on the oxide film. Fig. 16c presents the evolution of R_{pol} during immersion in 0.05 M NaCl solution, indicating the rate of corrosion process. R_{pol} reveals a stable behavior for the GPTMS coatings without nanocontainers. After the incorporation of the

loaded nanocontainers, R_{pol} takes values about four times higher than the blank coatings for the first 24 hours of immersion. Its values are fluctuated during the next 48 hours. This may be attributed to the contiguous release of 8HQ from the nanocontainers providing extended protection of the AA2024-T3 substrate. After 72 hours of immersion the polarization resistance is about 8 $k\Omega cm^2$ higher for the electro-deposited coating than the dip coated samples and about 20 $k\Omega cm^2$ higher than the coatings without the nanocontainers.

Although the incorporation of the nanocontainers improved the corrosion protection of all the films, it can be observed that electro-deposition provided slightly better coatings compare to the dip coating process, not only in homogeneity and adhesion but in of protection against corrosion as well. Though electro-deposited coatings with 2MB loaded nanocontainers provided similar protection to these with 8HQ as an inhibitor, the barrier properties of this film are poor and deteriorate fast.

Conclusion

Silane based sol-gel films have been developed on Al-2024-T3 and their corrosion protection properties were evaluated as a function of the type of the film (precursors) and the deposition procedure. GPTMS, DEDMOS and TMOMS were used as precursors. As GPTMS coatings provided the best corrosion protection it was chosen for further study. Studies on the time of electrochemical deposition, curing time and temperature were studied in order the corrosion protection properties of the coatings to be improved. The best results were obtained for curing temperature and time 90 °C and 24 hours, respectively. Ce-Ti nanocontainers loaded with 8HQ or 2MB were added into these coatings in different concentrations. The presence of the nanocontainers loaded with corrosion inhibitors improved the corrosion protection. EIS results give evidence of the appearance of another time constant corresponding to the barrier effect of the sol-gel coatings. However, additional studies have to be conducted towards this direction in order to understand the mechanism of the protection via nanocontainers and thus to optimise the procedure.

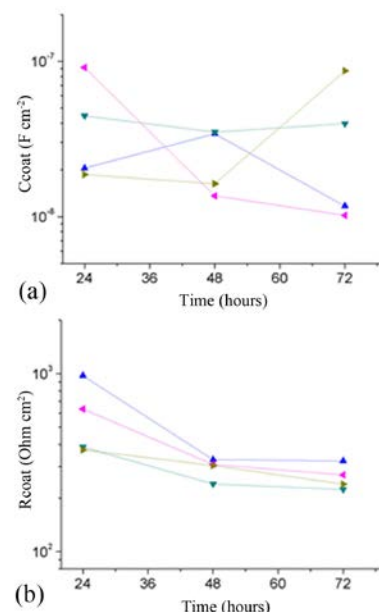


FIG. 15 EVOLUTION OF (A) COATING CAPACITANCE (CCOAT) AND (B) COATING RESISTANCE (RCOAT) AFTER EXPOSURE IN 0.05 M NaCl SOLUTION FOR GPTMS BASED COATINGS (▲) ELECTRO-DEPOSITED INCLUDING LOADED NANOCONTAINERS WITH 8HQ, (▼) DIP-COATED INCLUDING LOADED NANOCONTAINERS WITH 8HQ, (◄) ELECTRO-DEPOSITED INCLUDING LOADED NANOCONTAINERS WITH 2MB, (►) DIP-COATED INCLUDING NANOCONTAINERS WITH LOADED 2MB.

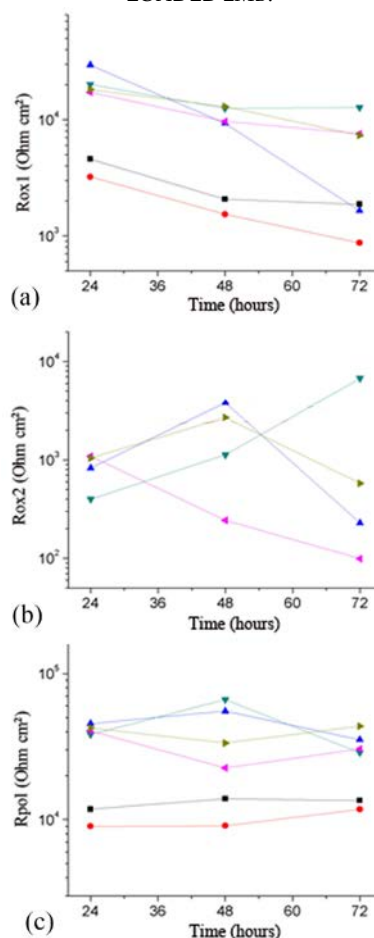


FIG. 16 EVOLUTION OF (A) OXIDE LAYER RESISTANCE (R_{ox1}), (B) INTERMEDIATE LAYER THAT DEVELOPS IN THE PRESENCE OF INHIBITOR (R_{ox2}) AND (C) POLARIZATION RESISTANCE (R_{pol}) FOR THE GPTMS BASED COATINGS (■) ELECTRO-DEPOSITED WITHOUT NANOCONTAINERS, (●) DIP-COATED WITHOUT NANOCONTAINERS, (▲) ELECTRO-DEPOSITED WITH NANOCONTAINERS LOADED WITH 8HQ, (▼) DIP-COATED WITH NANOCONTAINERS LOADED WITH 8HQ AND (◄) ELECTRO-DEPOSITED WITH NANOCONTAINERS LOADED WITH 2MB, (►) DIP-COATED WITH NANOCONTAINERS LOADED WITH 2MB, DURING 72 HOURS OF IMMERSION IN 0.05 M NaCl SOLUTION.

ACKNOWLEDGEMENT

This work was carried out in the context of the MULTIPROTECT project, funded by the European Community as contract N° NMP3-CT-2005-011783 under the 6th Framework Programme for Research and Technological Development.

The authors want to thanks "EADS" Deutschland for providing the samples of AA2024-T3. The abbreviation EADS stands for "European Aeronautical Defense and Space" Company.

REFERENCES

- [1] Raps, D., Hack, T., Kock, E., Beneke, M., Nuyken, O., "Replacement of Chromate Conversion Coatings – Promising Alternatives and Perspectives for the Aircraft Industry", *ATB Metall.*, vol. 45, pp. 402–410, 2006.
- [2] Twite, R.L., Bierwagen, G.P., "Review of Alternatives to Chromate for Corrosion Protection of Aluminum Aerospace Alloys" *Prog. Org. Coat.*, vol. 33, pp. 91-100, 1998.
- [3] Kuznetsov, Y.I., "Organic Inhibitors in Corrosion Metals", Plenum Press, New York, 1996.
- [4] Smit, M.A., Hunter, J.A., Sharman, Scamans, J.D.B., Sykes, G.M., Sykes, J.M., "Effect of Organic Additives on the Performance of Titanium-based Conversion Coatings", *Corros. Sci.* vol. 45 1903-1920, 2003.
- [5] Yang, X.F., Tallman, Gelling, D.E., , Bierwagen, V.J., Kasten, G.P., Berg, L.S., J., "Use of a Sol–gel Conversion Coating for Aluminum Corrosion Protection", *Surf. Coat. Tech.* vol. 140, pp. 44-50, 2001.
- [6] Yasuda, H., Chun, B.H., Cho, D.L., Lin, T., Yang, D.J., Antonelli, J.A., Interface-engineered Parylene C Coating for Corrosion Protection of Cold-rolled Steel, *Corrosion* vol. 52, pp. 169-176, 1996.
- [7] Shi, Z., Song, G., Atrens, A., Corrosion Resistance of Anodised Single Phased Mg alloys, *Surf. Coat. Tech.* vol. 201, pp. 492-503, 2006.
- [8] Paloumpa, I., Yfantis, A., Hoffman, P., Burkov, Y., Yfantis, D., Schimeiber, D., Mechanisms to Inhibit Corrosion of Al Alloys by Polymeric Conversion Coatings, *Surf. Coat. Tech.* vol. 180-181, pp. 308-312, 2004.
- [9] Tsirimpis, A., Kartsonakis, I.A., Danilidis, I., Kordas, G., "Synthesis of Conductive Polymeric Composite Coatings for Corrosion Protection Applications", *Prog. Org. Coat.* vol. 67, pp. 389-397, 2010.
- [10] Balaskas, A.C., Kartsonakis, I.A., Kordas, G.C., Cabral, A.M., Morais, P.J., "Influence of the Doping Agent on the Corrosion Protection Properties of Polypyrrole Grown on Aluminium Alloy 2024-T3", *Prog. Org. Coat.* vol. 71, pp. 181-187, 2011.
- [11] Balaskas, A.C., Kartsonakis, I.A., Snihirova, D., Montemor, M.F., Kordas, G., "Improving the Corrosion Protection Properties of Organically Modified Silicate – epoxy Coatings by Incorporation of Organic and Inorganic Inhibitors", *Prog. Org. Coat.* vol. 72, pp. 653-662, 2011.
- [12] Zheludkevich, M.L, Serra, R., Montemor, M.F., Yasakau, K.A., Miranda Salvado, I.M., Ferreira, M.G.S, "Nanostructured Sol–gel Coatings Doped with Cerium Nitrate as Pre-treatments for AA2024-T3 Corrosion Protection Performance", *Electrochim. Acta*, vol. 51, pp. 208-217, 2005.
- [13] Hoche, H., Scheerer, H., Probst, D., Broszeit, E., Berger, C., "Development of a Plasma Surface Treatment for Magnesium Alloys to Ensure Sufficient Wear and Corrosion Resistance", *Surf. Coat. Tech.* 174-175, pp. 1002-1023, 2003.
- [14] Rosero-Navarro, N.C., Pellice, S.A., Duran, A., Ceré, S., Aparicio, M., "Corrosion Protection of Aluminium alloy AA2024 with Cerium Doped Methacrylate-silica Coatings", *J Sol-Gel Sci Technol.* vol. 52, pp. 31–40, 2009.
- [15] Pepe, A., Aparicio, M., Cere, S., Duran, A., "Preparation And Characterization of Cerium Doped Silica Sol–gel Coatings on Glass and Aluminum Substrates, *J. Non-Cryst. Solids* vol. 348, pp. 162-171, 2004.

- [16] Lamaka, S.V., Zheludkevich, M.L., Yasakau, K.A., Montemor, M.F., Ferreira, M.G.S., "High Effective Organic Corrosion Inhibitors for 2024 Aluminium Alloy", *Electrochim. Acta* 52, pp. 7231-7247, 2007.
- [17] Yasakau, K.A., Zheludkevich, M.L., Karavai, O.V., Ferreira, M.G.S., "Influence of Inhibitor Addition on the Corrosion Protection Performance of Sol-gel Coatings on AA2024", *Prog. Org. Coat.* vol. 63, pp. 352-361, 2008.
- [18] Zheludkevich, M.L., Yasakau, K.A., Poznyak, S.K., Ferreira, M.G.S., "Triazole and Thiazole Derivatives as corrosion inhibitors for AA2024 Aluminium Alloy", *Corros. Sci.* vol. 47, pp. 3368-3383, 2005.
- [19] Khramov, A.N., Voevodin, N.N., Balbyshev, V.N., Donley, M.S., "Hybrid Organo-ceramic Corrosion Protection Coating with Encapsulated Organic Corrosion Inhibitors", *Thin Solid Films* vol. 447-448, pp. 549, 2004.
- [20] Shacham, R., Avnir, D., Mandler, D., "Electro-deposition of Methylated-sol-gel Films on Conducting Surfaces", *Adv. Mater.* vol. 11, pp. 384-388, 1999.
- [21] Sheffer, M., Groysman, A., Mandler, D., "Electro-deposition of Sol-gel Films on Al for Corrosion Protection", *Corros. Sci.*, vol. 45, pp. 2893-2904, 2003.
- [22] Mekeridis, E.D., Kartsonakis, I.A., Kordas, G.C., "Release Studies of Corrosion Inhibitors from Cerium Titanium Oxide Nanocontainers, *J. Nanopart. Res.* vol. 13, pp. 541-554, 2011.
- [23] Wang, D., *Prog. Sol-Gel Coatings On Metals For Corrosion Protection*, *Org. Coat.* vol. 64, pp. 327-338, 2009.
- [24] Morrison and Boyd, *Organic Chemistry*, 6th Edition, New York University, 1992.
- [25] Hu, J.M., Liu, L., Zhang, J.Q., Cao, C.N., *Electro-Deposition of Silane Films on Aluminum Alloys for Corrosion Protection*, *Prog. Org. Coat.* vol. 58, pp. 265-271, 2007.
- [26] Zheludkevich, M., Serra, R., Montemor, M.F., Ferreira, M.G.S., *Prolonged Release of the Corrosion Inhibitors*, *Electrochem. Commun.* vol. 7, pp. 836-840, 2005.